JC10 Rec'd PCT/PTO 1 7 DEC 2001

10/018764

Atty. Docket #: 0775/00025
(Basell-8)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INTERNATIONAL APPL. NO.: PCT/EP00/05651 :

INTERNATIONAL FILING DATE: -06/20/2000- :

APPLICANT: LUDWIG BÖHM ET AL :

SERIAL NO: TO BE ASSIGNED : ART UNIT:

FILED: -HEREWITH- : EXAMINER:

FOR: "POLYETHYLENE MOLDING MATERIAL AND :
PIPE PRODUCED THEREWITH WITH
IMPROVED MECHANICAL PROPERTIES" :

Commissioner for Patents
Box PCT
P.O. Box 2327
Arlington, VA 22202

"Express Mail" No.: ET481431450 Date: -DECEMBER 17, 2001-
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- Amy L. Hamm -
(Typed or printed name of mailing paper or fee)

(Signature of person mailing paper)

TRANSMITTAL OF APPLICATION PAPERS
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. §371
(37 CFR 1.494 OR 1.495)

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. §371.

2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371.

3. [X] This is an express request to begin national examination procedures (35 U.S.C. §371[f]) at any time rather than delay.

4. [X] A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.

5. [X] A copy of the International Application as filed (35 U.S.C. §371[c][2]) -- IN ENGLISH
    a. [X] is transmitted herewith (required when not transmitted by International Bureau) -with- One (1) Sheet of Drawing. See WIPO Publication
    b. [ ] has been transmitted by the International Bureau. WO 01/02480.
    c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).

6. [X] A (verified) translation of the International Application into the English language is enclosed. (See 5. above)

7. [ ] Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371[c][3])
    a. [ ] are transmitted herewith (required if not transmitted by the International Bureau).
    b. [ ] have been transmitted by the International Bureau.
    c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
    d. [ ] have not been made and will not be made.
    e. [ ] will be submitted with the appropriate surcharge.

8. [ ] A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371[c][3]) is enclosed or will be submitted with the appropriate surcharge.

9.   [X] An oath or declaration/power of attorney of the inventor(s) (35 U.S.C.
      §371[c][4]) is enclosed
      [X] and is attached to the translation of (or a copy of) the International
      Application.
      [ ] and is attached to the substitute specification.

10. [] A translation of at least the Annexes to the IPE Report under PCT Article 36 (35
      U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.

12. [X] An Assignment is enclosed for recording. A separate cover sheet in compliance
      with 37 CFR 3.28 and 3.31 is included.

13. [X] A FIRST preliminary amendment is enclosed.
      A SECOND or SUBSEQUENT preliminary amendment is enclosed.

14. [ ] A substitute specification (including claims, abstract, drawing) is enclosed.

15. [ ] A change of power of attorney and/or address letter is enclosed.

16. [X] Other items of information:

      [X]   This application is being filed pursuant to 37 CFR 1.494(c) or
               1.495(c), and any missing parts will be filed before expiration of--

                    [] 22 months from the priority date under 37 CFR
                    1.494(c), or

                    [X] 32 months from the priority date under 37 CFR
                    1.495(c).

      []   The undersigned attorney is authorized by the International applicant and
               by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c)
               or 1.495(c).

The following additional information relates to the International Application:

International Application No. PCT/EP00/05651   0775/00025

[X]   Receiving Office: EPO
[X]   IPEA (if filing under 37 CFR 1.495): EPO
[X]   Priority Claim(s) (35 USC §§ 119, 365):
          German Appln. 199 29 812.2 filed -June 30, 1999-.
[X] A copy of the International Search Report is

       [] enclosed.
       [x] attached to the copy of the International
           Application.

[X]   A copy of the Receiving Office Request Form
       [X] will follow
[X]   Form PCT/IB/306 (2) pages
[X]   Amendment of -April 17, 2001- (1) sheet, page -14-
[X]   Form PCT/IPEA/409 (In German) (7) sheets

The fee calculation is set forth on the next page of this Transmittal Letter.

10/018764
0775400025
531 Rec'd PCT   17 DEC 2001

FEE CALCULATION SHEET

[x]   A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee................................... $ 890.00

Total Number of claims in
excess of (20) times $18...................   -0-

Number of independent claims
in excess of (3) times $84.................   -0-

Fee for multiple dependent
claims $280................................   -0-

TOTAL FILING FEE... $ 890.00
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Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By _____
Richard M. Beck
Reg. No. 22,580
CONNOLLY BOVE LODGE & HUTZ LLP
1220 Market Street
P.O. Box 2207
Wilmington, Delaware 19899
Tel. (302) 658-9141

RMB/alh (9086*187)
Enclosures
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0775/00025

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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LUDWIG BOHM ET AL   :

SERIAL NO: : **ART UNIT:**

FILED: -HEREWITH-   : **EXAMINER:**

FOR: "POLYETHYLENE MOLDING MATERIAL   :
AND PIPE PRODUCED THEREWITH WITH
IMPROVED MECHANICAL PROPERTIES"   :

                                                       :

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- Amy L. Hamm -

(Typed or printed name) of   **(Signature of person**
person mailing paper or fee)   **mailing paper or fee)**

PRELIMINARY AMENDMENT

Sir:

     Prior to any action on the merits of the accompanying
new patent application, kindly amend the application as
follows:

In the Claims:

     Please amend claims 4-10 as follows. The amended claims
are shown in their final form below. An underline/bracket
version of the amended claims is provided as Appendix A.

1

4. (Amended) Pipe according to Claim 2, characterized in that has been produced from an ethylene polymer having a bimodal molecular weight distribution which comprises co-monomers having from 4 to 10 carbon atoms in an amount of from 2.5 to 4% by weight in the relatively high-molecular-weight fraction B.

5. (Amended) Pipe according to Claim 3, characterized in that the low-molecular-weight fraction of the ethylene polymer has a melt flow index $MFI_{2.16/190°C}$ in the range from 200 to 800 g/10 min, preferably from 250 to 450 g/10 min.

6. (Amended) Pipe according to Claim 3, characterized in that the ethylene polymer has a melt flow index $MFI_{5/190°C}$ of ≤ 0.19 dg/min.

7. (Amended) Pipe according to Claim 2, characterized in that it has a notched impact strength NIS_{ISO}, measured in accordance with ISO 179 (DIN 53453), of at least 25 mJ/mm^2 at -20°C and of at least 40 mJ/mm^2 at +23°C.

8. (Amended) Pipe according to Claim 2, characterized in that it has a resistance to rapid crack growth, measured in accordance with ISO/DIS 13477 on a pipe in pressure class PN 10 having a diameter of 110 mm (S4 test), of ≥ 20 bar.

9. (Amended) Use of a pipe according to Claim 2 for the transport of gases, in particular for the transport of natural gas.

-2-

10. (Amended) Use of a pipe according to Claim 2
for the transport of water.

R E M A R K S

Claims 4-10 have been amended to refer to only one
preceding claim. Each of the dependent claims, as amended,
now depends on only one preceding claim. Therefore no
additional fee is required for multiple dependency.

Prompt, favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By _Richard M. Beck_

Richard M. Beck
Registered No. 22,580
1220 Market Street
P.O. Box 2207
Wilmington, Delaware 19899

RMB/alh
(9086*187)

Enclosure: APPENDIX A
             Underline/Bracket
             Version of amended claims

APPENDIX A

Underline/Bracket Version of Amended

Claims

4. (Amended) Pipe according to Claim 2 [or 3], characterized in that it has been produced from an ethylene polymer having a bimodal molecular weight distribution which comprises comonomers having from 4 to 10 carbon atoms in an amount of from 2.5 to 4% by weight in the relatively high-molecular-weight fraction B.

5. (Amended) Pipe according to Claim 3 [or 4], characterized in that the low-molecular-weight fraction of the ethylene polymer has a melt flow index $MFI_{2.16/190°C}$ in the range from 200 to 800 800 g/10 min, preferably from 250 to 450 g/10 min.

6. (Amended) Pipe according to [one of Claims 3 to 5] Claim 3, characterized in that the ethylene polymer has a melt flow index $MFI_{5/190°C}$ of $\leq$ 0.19 dg/min.

7. (Amended) Pipe according to [one of Claims 2 to 6] Claim 2, characterized in that it has a notched impact strength NIS_{ISO}, measured in accordance with ISO 179 (DIN 53453), of at least 25 mJ/mm^2 at -20°C and of at least 40 mJ/mm^2 at +23°C.

8. (Amended) Pipe according to [one of Claims 2 to 7] Claim 2, characterized in that it has a resistance to rapid crack growth, measured in accordance with ISO/DIS 13477 on a pipe in pressure class PN 10 having a diameter of 110 mm (S4 test), of $\geq$ 20 bar.

9. (Amended) Use of a pipe according to [one of Claims 2 to 8] Claim 2 for the transport of gases, in particular for the transport of natural gas.

10. (Amended) Use of a pipe according to [one of Claims 2 to 8] Claim 2 for the transport of water.

-4-

POLYETHYLENE MOLDING MATERIAL
AND PIPE PRODUCED THEREWITH
WITH IMPROVED MECHANICAL PROPERTIES

Ludwig Böhm
Joachim Berthold
Johannes-Friedrich Enderle
Elke Damm

-and-

Ulrich Schulte

INTERNATIONAL APPLICATION

IN ENGLISH

PCT/EP00/05651   ....   IFD: –June 20, 2000–
-with-

One (1) Sheet of Drawing

0775/00025   ....   (9086*187)
(Basell-8)

Title: Polyethylene molding material and pipe produced
therewith with improved mechanical properties

The present invention relates to a polyethylene molding
material having a bimodal molecular weight
5   distribution, and to a high-strength pipe produced from
this molding material.

Polyethylene is widely used for the production of
pipes, for example for gas- and water-transport
systems, since a material having particularly high
10   mechanical strength, high corrosion resistance and
absolutely reliable long-term stability is required for
such pipes. Numerous publications describe materials
having an extremely wide variety of properties and
processes for their production.

15   EP-A-603 935 has already described a molding material
based on polyethylene which has a bimodal molecular
weight distribution and is also said to be suitable,
inter alia, for the production of pipes. However, pipes
produced from the molding materials in accordance with
20   this reference are unsatisfactory with respect to their
long-term resistance to internal pressure, their stress
cracking resistance, their low-temperature notched
impact strength and their resistance to rapid crack
growth.

25   In order to achieve pipes having balanced mechanical
properties and thus an optimum property combination, it
is necessary to employ a raw material which has an even
broader molecular weight distribution. A raw material
of this type is described in US Patent 5,338,589 and is
30   produced using a highly active catalyst which is
disclosed in WO 91/18934 and in which the magnesium
alkoxide is employed as a gel-form suspension.
Surprisingly, it has been found that the use of this
material in moldings, in particular in pipes, enables a

simultaneous improvement on the one hand in the properties of rigidity and creep tendency, which are usually contradictory in partially crystalline thermoplastics, and on the other hand stress cracking

5   resistance and toughness.

EP-A-0 739 937 has already disclosed a pipe which has mechanical properties which meet the very highest demands made by consumer associations and have resulted in classification of this pipe in quality class "PE

10   100" in accordance with ISO/DIS 9080.

The object of the present invention was the development of a polyethylene molding material with which even better strength of the pipes produced therewith can be achieved compared with the known pipe material in

15   strength class PE 100 in accordance with ISO/DIS 9080.

This object is achieved by a molding material according to Claim 1. The invention furthermore also relates to a pipe produced from this molding material having really excellent mechanical properties, and to its use for the

20   construction of gas and water lines.

The polyethylene molding material according to the invention has a density at a temperature of 23°C in the range $\geq$ 0.948 as a natural product, i.e. without addition of dye, and $\geq$ 0.959 g/cm^3 as a black-colored

25   product having a carbon black content in the range from 2 to 5% by weight, based on the total weight of the black-colored product, and has a broad bimodal molecular weight distribution, in which the ratio of the weight of the low-molecular-weight fraction to the

30   weight of the relatively high-molecular-weight fraction is in the range from 0.5 to 2.0, preferably from 0.8 to 1.8. The polyethylene may comprise small proportions of up to 5% by weight of further monomer units having from 4 to 10 carbon atoms. Examples of such comonomers are

35   1-butene, 1-pentene, 1-hexene or 4-methyl-1-pentene.

The bimodality can be described as a measure of the position of the centers of the two individual molecular weight distributions with the aid of the viscosity numbers (VN) in accordance with ISO/R 1191 of the polymers formed in two successive polymerization steps. The VN_1 of the low-molecular-weight polyethylene formed in the first polymerization step is from 40 to 90 cm^3/g, while VN_{total} of the end product is in the range from 300 to 450 cm^3/g. VN_2 of the relatively high-molecular-weight polyethylene formed in the second polymerization step can be calculated from the following mathematical formula:

$$VN_2 = \frac{VN_{total} - w_1 \cdot VN_1}{1 - w_1}$$

where w_1 stands for the proportion by weight of the low-molecular-weight polyethylene formed in the first step, measured in % by weight, based on the total weight of the polyethylene having a bimodal molecular weight distribution formed in the two steps. The value calculated for VN_2 is normally in the range from 500 to 2000 cm^3/g.

The molding material according to the invention has long-term properties which even go beyond the requirement for quality class PE 100 in accordance with ISO/DIS 9080 of 10.0 MPa after 50 a as LCL (lower critical confidence limit), determined by the extrapolation method. Surprisingly, the polyethylene molding material according to the invention achieves an extremely high resistance to slow crack growth with the requisite relatively high rigidity and at relatively high yield stress. This high stress cracking resistance is evident from the fact that brittle fracture was not observed in the LTHS (long term hydrostatic strength) test within a time interval of 33,000 h at a temperature for 80°C on pipes produced from the molding material according to the invention.

In the LTHS test, the service life of the pipes without brittle fracture is determined by extrapolation to 50 years. Owing to the extremely high stress cracking resistance achieved by the molding material according to the invention, the ductile line in the creep diagram, with the aid of which the service life is extrapolated to 50 years, is very flat. Consequently, an internal pressure of 12.5 MPa arises in accordance with this test method for pipes produced from the molding material according to the invention at a test temperature of 23°C and a service life of 50 years, which accordingly results in a new quality class, PE 125.

The extrapolation curve at 23°C can be described mathematically by the following equation:

$$\sigma = K \cdot t_{failure}^{-\eta}$$

For the standard values $K = 15.6$ and $\eta = -0.017$, the following values arise through extrapolation for pipes produced from the molding material according to the invention:

$t_{failure}$	10 h	10,000 h	50 years
σ	15.0	13.3	12.5

The polyethylene is obtained by polymerization of the monomers in suspension, in solution or in the gas phase at temperatures in the range from 20 to 120°C, a pressure in the range from 2 to 60 bar and in the presence of a Ziegler catalyst composed of a transition-metal compound and an organoaluminium compound. The polymerization is carried out in two successive steps, the molecular weight of the polyethylene being regulated in each step with the aid of hydrogen.

The polyethylene molding material according to the invention may, besides the polyethylene, also comprise further additives. Such additives are, for example, heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, peroxide-destroying compounds, basic costabilizers in amounts of from 0 to 10% by weight, preferably from 0 to 5% by weight, but also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistatics, blowing agents or combinations of these in total amounts of from 0 to 50% by weight.

The pipe according to the invention is produced by firstly plasticating the polyethylene molding material in an extruder at temperatures in the range from 200 to 250°C and then extruding the molding material through an annular die and cooling it. Pipes of the type according to the invention are generally suitable for all pressure classes in accordance with DIN 8074.

For conversion into pipes, it is possible to employ both conventional single-screw extruders having a smooth feed zone and also high-performance extruders having a finely grooved barrel and forced-conveying feed. The screws are typically designed as decompression screws with a length of from 25 to 30 D (D = $\varnothing$). The decompression screws have a metering zone in which temperature differences in the melt are compensated and in which the aim is for the relaxation stresses produced by shearing to be relaxed.

The melt coming from the extruder is firstly distributed over an annular cross section via conically arranged holes and then fed to the mandrel/die ring combination via a spiral mandrel melt distributor or a screen pack. In addition, restrictor rings or other design elements for smoothing out the melt flow may, if necessary, be installed before the die exit.

The calibration and cooling are advantageously carried out by vacuum calibration up to large pipe diameters. The actual shaping is carried out using slotted calibration sleeves, which, for better heat

5 dissipation, are made of non-ferrous metal. A water film supplied in the inlet ensures rapid cooling of the surface of the pipe below the crystalline melting point and additionally serves as lubricating film for reducing frictional forces. The total length L of the

10 cooling zone is set under the assumption that a melt having a temperature of 220°C is to be cooled with the aid of water having a temperature of from 15 to 20°C to the extent that the temperature of the pipe inside surface is at most 85°C.

15 The stress cracking resistance is a feature which is already known from EP-A 436 520. The process of slow crack growth can be significantly influenced by molecular structural parameters, such as molecular weight distribution and comonomer distribution. The

20 number of so-called tie molecules is firstly determined by the chain length of the polymer. The morphology of partially crystalline polymers is in addition established by the incorporation of comonomers, since the thickness of crystalline lamellae can be influenced

25 by the introduction of short-chain branches. This means that the number of tie molecules in copolymers is greater than in homopolymers having a comparable chain length.

➤ The stress cracking resistance of the pipe

30 according to the invention is determined by an internal measurement method. This laboratory method has been described by M. Fleißner in Kunststoffe 77 (1987), p. 45 et seq. This publication shows that there is a correlation between the determination of slow crack

35 growth in the creep test on test bars notched all round and the brittle branch of the long term hydrostatic strength test in accordance with ISO 1167. A shortening

of the time to failure is achieved by shortening the crack initiation time by the notches (1.6 mm/razor blade) in ethylene glycol as stress cracking-promoting medium at a temperature of 80°C and a tensile stress of 5 MPa. The samples are produced by cutting three test specimens having the dimensions 10 x 10 x 90 mm out of a pressed sheet with a thickness of 10 mm. The test specimens are notched all round in the center using a razor blade in a notching device made specifically for the purpose (see Figure 5 in the above-mentioned publication). The notch depth is 1.6 mm.

➤ The fracture toughness of the pipe according to the invention is likewise determined by an internal measurement method on test bars having the dimensions 10 x 10 x 80 mm which have been cut out of a pressed sheet with a thickness of 10 mm. Six of these test bars are notched in the center using a razor blade in the notching device already mentioned. The notch depth is 1.6 mm. The measurement is carried out largely corresponding to the Charpy measurement method in accordance with ISO 179 with different test specimens and a different impact geometry (distance between the supports). All test specimens are conditioned to the measurement temperature of 0°C over a period of from 2 to 3 hours. A test specimen is then quickly placed onto the support of a pendulum impact tester in accordance with ISO 179. The distance between the supports is 60 mm. The drop of the 2 J hammer is initiated, the drop angle being set to 160°, the pendulum length to 225 mm and the impact velocity to 2.93 m/sec. For evaluation of the measurements, the quotient of consumed impact energy and initial cross-sectional area at the notch a_{FM} in mJ/mm^2 is calculated. Only values for complete fracture and hinge fracture may serve as the basis for a joint mean (see ISO 179).

➤ The notched impact strength$_{ISO}$ is measured in accordance with ISO 179. The dimension of the sample is

10 x 4 x 80 mm, with a V-notch having an angle of 45°, a depth of 2 mm and a notch base radius of 0.25 mm being grooved in.

➤   The flexural creep modulus is measured as the one-
5   minute value in accordance with DIN 54852-Z4.

➤   The S4 test (small scale steady state test) serves to determine the resistance of the pipe to rapid crack propagation and is carried out on pipes with the dimension PN 10 having a diameter of 110 mm. The
10   precise method is described in ISO/DIS 13477. This method determines the critical pressure p_c in bar above which the pipe under this pressure p_c cracks longitudinally over the entire length.

The following working examples are intended to depict
15   the invention still more clearly for the person skilled in the art.

Example 1 (according to the invention):

A polyethylene molding material was produced using a Ziegler catalyst and in accordance with the procedure
20   of WO 91/18934 maintaining the operating conditions indicated below in Table 1:

Table 1

	Reactor I Capacity: 120 l	Reactor II Capacity: 120 l
Temperature	83°C	83°C
Catalyst feed	0.8 mmol/h	----
Cocatalyst feed	15 mmol/h	30 mmol/h
Dispersion medium (diesel oil)	25 l/h	50 l/h
Ethylene	9.5 kg/h	10 kg/h
1-Hexene	0 ml/h	913 ml/h
Hydrogen in the gas phase	80% by vol.	0.7% by vol.
Total pressure	8.9 bar	2.0 bar

The polyethylene molding material produced in this way had a melt flow index $MFI_{5/190°C}$ of 0.18 dg/min, measured in accordance with ISO 11 33, and a density d of

5   0.950 g/cm^3. For even better characterization, the polyethylene was subjected to a preparative TREF analysis (Temperature Rising Elution Fractionation). This analytical method is a very useful tool for determining the comonomer distribution in partially

10   crystalline polyethylene and has been published by L. Wild and T. Ryle under the title: "Crystallization distribution in polymers: a new analytical technique" in Poly. Prep. Am Chem. Soc., - Polym. Chem Div., 18, 182 (1977). In accordance with this analytical method,

15   the polymer to be investigated is dissolved in p-xylene, deposited on an inorganic support material and fractionated little by little therefrom using p-xylene at continuously rising temperatures, with the less crystalline fractions dissolving at lower temperatures

and the more highly crystalline fractions dissolving at higher temperatures. In this way, it is possible to separate a partially crystalline polymer into different amount fractions, depending on the thickness of the 5 crystalline lamellae. The various fractions can then themselves be again investigated for their molecular weight distribution by the GPC method (Gel Permeation Chromatography).

The diagram attached as **Figure 1** shows the result of a 10 combined TREF/GPC analysis with the polyethylene molding material according to the invention.

The polyethylene produced as described above in accordance with Example 1 was firstly dissolved in p-xylene (boiling point: 138°C) as indicated above and 15 then deposited on a Chromosorb P support material by cooling. Fractions were then formed by elution at temperatures of 60, 70, 78, 83, 86, 89, 93, 100 and 110°C. A GPC analysis was then carried out with the fraction at 78°C ± 3 K and the polymer fraction 20 dissolved therein. Peak 1 shows the low-molecular-weight, highly crystalline PE fraction which is soluble at 78°C, with a low thickness of the crystalline lamellae, while peak 2 is caused by a fraction of greater molecular weight, but at the same time a high 25 proportion of comonomer incorporation and thus again lower crystallinity. This product fraction coming under peak 2 is responsible for the high number of so-called "tie molecules" between the crystalline lamellae and thus for the extremely high stress cracking resistance 30 of the pipe produced from the molding material according to the invention.

The polyethylene produced as described above in accordance with Example 1 was plasticated in an extruder having a diameter of 48 mm and a length 35 corresponding to 24.4 times the diameter (117.12 cm) at a temperature of 227°C and subsequently extruded

through an annular die having an external diameter of 32.1 mm and a mandrel having a diameter of 26.5 mm to give a pipe having a diameter of 32.1 mm and a wall thickness of 3.08 mm with the aid of vacuum calibration. The cooling was carried out in a cooling bath having a length of 3 m which was held at a temperature of 15°C. The properties measured on the finished pipe are shown in **Table 2** below.

Comparative Example:

A pipe was produced from polyethylene in accordance with the details in Example 1 of EP-A-739 937. The properties measured on the pipe are likewise shown in Table 2 below.

The abbreviations for the physical properties in Table 2 have the following meanings:

- FCM = flexural creep modulus, measured in accordance with ISO 54852-Z4 in N/mm^2 as the one-minute value,

- FT = fracture toughness measured by the internal measurement method described above at 0°C in mJ/mm^2,

- NIS_{Iso} = notched impact strength, measured in accordance with ISO 179/DIN 53453 in mJ/mm^2 at -20°C and at +23°C,

- SCR = stress cracking resistance measured by the internal measurement method of M. Fleißner in h,

- PAB = processability, measured as extruder throughput in an extruder having a diameter D of 48 mm and a length L of 24.4·D at a constant screw speed of 80 revolutions per minute in kg/h,

    — p_c = resistance to rapid crack growth, measured by the S4 test in bar on pipes in pressure class PN 10 having a diameter of 110 mm.

Table 2

	Example 1	Comparison
FCM	1400	1304
FT	10.0	8.8
NIS_{Iso} (+23/-20°C)	40/26	39.2/24.1
SCR	>> 1500	>> 1500
PAB	28	28.2
p_c	> 25	> 25
LTHS extrapol. 23°C LCL 50 a	12.5	11.1

The measurement values clearly show that the pipe according to the invention had much better strength properties and could also be processed better during production.

* * * * *

Patent Claims

1. Polyethylene molding material having a bimodal molecular weight distribution which has an overall density of ≥ 0.948 g/cm^3 and an $MFI_{190/5}$ of ≤ 0.2 dg/min, characterized in that it comprises an amount of from 35 to 65% by weight of low-molecular-weight ethylene homopolymer A which has a viscosity number VN_A in the range from 40 to 90 cm^3/g, a melt flow index $MFI_{190/2.16\ A}$ in the range from 40 to 2000 dg/min and a density d_A of ≥ 0.965 g/cm^3, and an amount of from 35 to 65% by weight of high-molecular-weight ethylene copolymer B which has a viscosity number VN_B in the range from 500 to 2000 cm^3/g, a melt flow index $MFI_{190/5\ B}$ in the range from 0.02 to 0.2 dg/min and a density d_B in the range from 0.922 to 0.944 g/cm^3, and in that the fraction obtained during a preparative TREF analysis at a temperature of 78°C $\pm$ 3 K using p-xylene has an average molecular weight of $\geq 200,000$ g/mol.

2. Pipe produced from a polyethylene molding material according to Claim 1, characterized in that it has a stress cracking resistance of ≥ 1500 h and a fracture toughness FT of ≥ 9 mJ/mm^2.

3. Pipe according to Claim 2, characterized in that it has a flexural creep modulus, measured in accordance with DIN 54852-Z4, of ≥ 1350 N/mm^2.

4. Pipe according to Claim 2 or 3, characterized in that it has been produced from an ethylene polymer having a bimodal molecular weight distribution which comprises comonomers having from 4 to 10 carbon atoms in an amount of from 2.5 to 4% by weight in the relatively high-molecular-weight fraction B.

5. Pipe according to Claim 3 or 4, characterized in that the low-molecular-weight fraction of the ethylene polymer has a melt flow index $MFI_{2.16/190°c}$ in the range

from 200 to 800 g/10 min, preferably from 250 to 450 g/10 min.

6. Pipe according to one of Claims 3 to 5, characterized in that the ethylene polymer has a melt flow index $MFI_{5/190°C}$ of ≤ 0.19 dg/min.

7. Pipe according to one of Claims 2 to 6, characterized in that it has a notched impact strength NIS_{ISO}, measured in accordance with ISO 179 (DIN 53453), of at least 25 mJ/mm^2 at -20°C and of at least 40 mJ/mm^2 at +23°C.

8. Pipe according to one of Claims 2 to 7, characterized in that it has a resistance to rapid crack growth, measured in accordance with ISO/DIS 13477 on a pipe in pressure class PN 10 having a diameter of 110 mm (S4 test), of ≥ 20 bar.
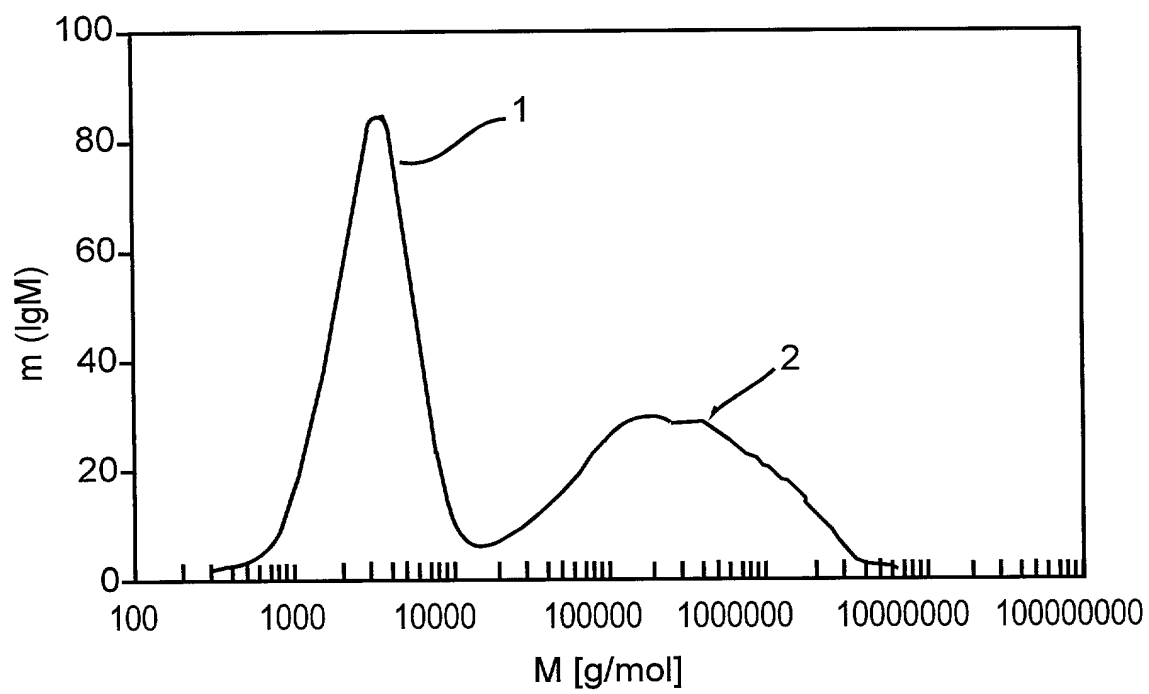
9. Use of a pipe according to one of Claims 2 to 8 for the transport of gases, in particular for the transport of natural gas.

10. Use of a pipe according to one of Claims 2 to 8 for the transport of water.

* * * * * * *

COMBINED DECLARATION AND POWER OF ATTORNEY	Attorney Docket No. 0775/00025

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **POLYETHYLENE MOLDING MATERIAL AND PIPE PRODUCED THEREWITH WITH IMPROVED MECHANICAL PROPERTIES** the specification of which

was filed as PCT international application number PCT/EP00/05651 on June 20, 2000

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)   Priority Claimed

| 199 29 812.2 | Germany | 30 June 1999 | X | |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |

| | | | | |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

(Application No.)	(filing date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

PCT/EP00/05651	20 June 2000	Published (WO 01/02480)
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

In the matter of the above-identified application, please recognize the attorneys associated with **CUSTOMER NUMBER 23416**; all of CONNOLLY BOVE LODGE & HUTZ LLP, as attorneys with full power of substitution to prosecute this application and conduct all business in the Patent and Trademark Office connected therewith.

Send Correspondence To: **Connolly Bove Lodge & Hutz LLP** P.O. Box 2207 Wilmington, Delaware 19899-2207	Direct Telephone Calls To: (302) 658-9141

FULL NAME OF SOLE OR FIRST INVENTOR	INVENTOR'S SIGNATURE	DATE
Ludwig Böhm	*Ludwig Böhm*	24/10/2001
RESIDENCE	CITIZENSHIP	
Leonhardstraße 36, D-65795 Hattersheim, Germany *DE*	German	
POST OFFICE ADDRESS		
Basell Polyolefine GmbH, Industriepark Höchst, Patent department, Building E413, D-65926 Frankfurt/Main, Germany		

FULL NAME OF SECOND JOINT INVENTOR IF ANY	INVENTOR'S SIGNATURE	DATE
Joachim Berthold	*[signature]*	07/11/2001
RESIDENCE	CITIZENSHIP	
Am Flachsland 54, D-65779 Kelkheim, Germany *DE*	German	
POST OFFICE ADDRESS		
Basell Polyolefine GmbH, Industriepark Höchst, Patent department, Building E413, D-65926 Frankfurt/Main, Germany		

FULL NAME OF THIRD JOINT INVENTOR IF ANY	INVENTOR'S SIGNATURE	DATE
Johannes-Friedrich Enderle	*[signature]*	07/11/2001
RESIDENCE	CITIZENSHIP	
Spohrstraße 26, D-60318 Frankfurt, Germany *DE*	German	
POST OFFICE ADDRESS		
Basell Polyolefine GmbH, Industriepark Höchst, Patent department, Building E413, D-65926 Frankfurt/Main, Germany		

FULL NAME OF FOURTH JOINT INVENTOR IF ANY	INVENTOR'S SIGNATURE	DATE
Elke Damm	*Elke Damm*	5. 11. 2001
RESIDENCE	CITIZENSHIP	
Adalbert-Stifter-Straße 11, D-60431 Frankfurt, Germany *DE*	German	
POST OFFICE ADDRESS		
Basell Polyolefine GmbH, Industriepark Höchst, Patent department, Building E413, D-65926 Frankfurt/Main, Germany		

FULL NAME OF FIFTH JOINT INVENTOR IF ANY	INVENTOR'S SIGNATURE	DATE
Ulrich Schulte	*[signature]*	25. 10. 2001
RESIDENCE	CITIZENSHIP	
Hornauer Straße 120 a, D-65779 Kelkheim, Germany *DE*	German	
POST OFFICE ADDRESS		
Basell Polyolefine GmbH, Industriepark Höchst, Patent department, Building E413, D-65926 Frankfurt/Main, Germany		

FULL NAME OF SIXTH JOINT INVENTOR IF ANY	INVENTOR'S SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		

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